The Crystal Structure and Luminescence Properties of Europium(II) Haloborates

Ken-ichi MACHIDA, Gin-ya ADACHI,* Yoshikazu MORIWAKI, and Jiro SHIOKAWA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

(Received May 10, 1980)

The crystal structures of $Eu_2B_5O_9X$ (X=Cl and Br) were determined by the method of X-ray diffraction analysis and refined by the least-square method to give $R=0.054$ for 1967 observed reflections of $Eu_2B_5O_9Cl$ and $R=0.047$ for 1979 observed reflections of $Eu_2B_5O_9Br$. These haloborates are isostructural and belong to the orthorhombic (pseudotetragonal) system, with the *Pnn*2 space group and with four formula units in a cell of those dimensions: $a=11.364(3)$, $b=11.301(3)$, and $c=6.504(2)$ Å for $Eu_2B_5O_9Cl$, and $a=11.503(3)$, $b=11.382(3)$, and $c=6.484(2)$ Å for $Eu_2B_5O_9Br$. The structure consists of a three-dimensional $(B_5O_9)_\infty$ network, the B_5O_{12} groups of three BO_4 tetrahedra and two BO_3 triangles being linked together with one another. The Eu and X atoms are located alternately in tunnels of the $(B_5O_9)_\infty$ network extending along the c axis. Each Eu atom is surrounded by two X atoms and seven O atoms, and is isolated from the neighboring Eu atoms attributable to borate units and X atoms. This arrangement of anions around Eu atoms relates to the fact that the Eu^{2+}-activated phosphors of alkaline earth analogs give emissions with a high quantum efficiency.

Phosphors of Eu^{2+}-activated alkaline earth compounds give emissions based on the $4f^7-4f^65d$ transition or the $4f^7-4f^7$ transition of the Eu^{2+} ion.[1] Recently we have reported that the quantum efficiencies of compounds in the $EuO-B_2O_3$ system and their Eu^{2+}-activated strontium analogs depend greatly on the structural frameworks of borate units.[2] In the ternary system $EuO-EuX_2-B_2O_3$ (X=Cl and Br), $Eu_2B_5O_9$-type compounds have been obtained in attempts to prepare their boracite-type compounds,[3] they are paramagnetic and give blue emissions based on the $4f^7-4f^65d$ transition of the Eu^{2+} ion.[4] The compounds obtained by the dilution of the Eu^{2+} ions in the $Eu_2B_5O_9X$ matrix with alkaline-earth cations have been found to be efficient photoluminescent materials.[5] In this paper, we wish to report on the crystal structure of $Eu_2B_5O_9X$ and discuss their luminescence properties on the basis of X-ray structural analysis.

Experimental

Sample Preparation. Single crystals of $Eu_2B_5O_9X$ were prepared as follows: mixtures of EuB_2O_4 and B_2O_3 containing a large excess of EuX_2 as a flux were heated on molybdenum boats above the congruent melting points of haloborates (about 1100 °C) for 1—2 h in He gas; the molten samples were then allowed to cool at a rate of 3—5 °C/h. When the unreactive EuX_2 was then removed from the samples with washing with water, light-yellow crystals were obtained. Their crystal habits were prismatic for $Eu_2B_5O_9Cl$ and needle-like for $Eu_2B_5O_9Br$.

The Eu^{2+}-activated strontium haloborates, $Sr_2B_5O_9Cl$: Eu^{2+} and $Sr_2B_5O_9Br$: Eu^{2+}, were obtained by the following standard ceramic technique: appropriate amounts of SrX_2, H_3BO_3, and $SrCO_3$: Eu^{3+}, coprecipitated from a dilute HCl solution of $Sr(NO_3)_2$ and Eu_2O_3 (99.99%) by the slow addition of a $(NH_4)_2CO_3$ solution, were fully mixed, pelletized, and heated at 950 °C for 2 h in a stream of a reducing atmosphere, H_2.

Optical Measurements. The ultraviolet luminescence spectra were measured according to a technique described elsewhere.[2]

X-Ray Data Collection. Preliminary Weissenberg photographs and the Patterson syntheses showed that $Eu_2B_5O_9X$ belongs to the orthorhombic (pseudotetragonal) system, with a noncentrosymmetric space group *Pnn*2 and with $Z=4$.† The accurate cell parameters of $Eu_2B_5O_9Cl$ and $Eu_2B_5O_9Br$ were determined by least-square treatments of the X-ray powder diffraction patterns (Cu $K\alpha_1$), calibrated with high purity silicon. The crystal data are summarized in Table 1.

TABLE 1. CRYSTAL DATA

	$Eu_2B_5O_9Cl$	$Eu_2B_5O_9Br$
F.W.	537.43	581.88
Orthorhombic		
Pnn2 ($0kl$, $k+l=2n+1$; $h0l$, $h+l=2n+1$)		
a/Å	11.364(3)	11.503(3)
b/Å	11.301(3)	11.382(3)
c/Å	6.504(2)	6.484(2)
V/Å^3	835.2(5)	848.9(4)
D_m/g cm^{-3}	4.30	4.53
D_x/g cm^{-3}	4.28	4.55
Z	4	4
$F(000)$	960	1032
Crystal size/mm^3	$0.14\times0.08\times0.17$	$0.10\times0.10\times0.20$
μ(Mo $K\alpha$)/mm^{-1}	15.283	19.264

The intensity data were measured on a Rigaku Denki automated four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) monochromated with graphite. The ω-2θ scan technique was employed with a scanning rate of 4°/min. All the independent reflections were collected up to $2\theta=70°$. Three standard reflections were monitored every 50 or 60 reflections; no apparent decay in intensity was detected. The reflections with $F_o>3\sigma(F_o)$ were considered as observed: 1967 and 1979 observed reflections were obtained for $Eu_2B_5O_9Cl$ and $Eu_2B_5O_9Br$ respectively. The Lorentz and polarization corrections were applied, but the absorption correction was not.

Structure Determination and Refinements. The structures of europium (II) haloborates were solved by the conventional heavy-atom method and were refined by the method of block-diagonal least-squares (*HBLS*-V program[6]), the minimized function being $\sum w(|F_o|-|F_c|)^2$. From the three-dimensional Patterson syntheses, the coordinates of Eu and X atoms were determined: Eu(1) and Eu(2) atoms can be located on the general positions (4*c* site), while X(1) and X(2) atoms occupy

† The symmetry of $Eu_2B_5O_9Cl$ has been erroneously reported as tetragonal in a previous paper.[4]

TABLE 2. FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Eu_2B_5O_9Cl$, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Europium atoms ($\times 10^4$)

The form of the anisotropic thermal parameters ($\times 10^5$) is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Eu(1)	2523(7)	475(6)	0	120(3)	106(3)	278(10)	25(6)	−61(12)	−61(14)
Eu(2)	255(6)	2403(6)	6624(12)	74(3)	149(3)	246(9)	−11(6)	−71(14)	17(17)

(b) Non-europium atoms ($\times 10^3$)

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
Cl(1)	0	0	862(6)	1.08(7)	O(7)	182(10)	269(10)	939(10)	0.21(11)
Cl(2)	0	500	613(6)	1.03(7)	O(8)	421(10)	207(10)	510(12)	0.53(12)
O(1)	244(10)	318(10)	594(10)	0.31(12)	O(9)	232(10)	114(10)	576(11)	0.46(12)
O(2)	211(10)	427(10)	1191(11)	0.60(13)	B(1)	274(14)	325(13)	809(15)	0.25(16)
O(3)	279(10)	225(10)	1255(10)	0.38(12)	B(2)	187(12)	299(12)	1162(20)	0.29(14)
O(4)	77(11)	270(11)	1263(11)	0.61(13)	B(3)	292(14)	217(13)	479(15)	0.31(16)
O(5)	286(11)	451(10)	853(12)	0.64(13)	B(4)	457(22)	231(21)	712(23)	1.40(27)
O(6)	384(12)	262(11)	856(12)	0.78(14)	B(5)	251(16)	497(15)	1035(15)	0.57(19)

TABLE 3. FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Eu_2B_5O_9Br$, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Heavy atoms ($\times 10^4$)

The form of the anisotropic thermal parameters ($\times 10^5$) is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Eu(1)	2547(6)	501(6)	0	113(3)	118(3)	396(9)	35(6)	−62(11)	−52(12)
Eu(2)	307(6)	2374(6)	6572(10)	92(3)	140(3)	360(9)	−13(5)	−84(12)	7(15)
Br(1)	0	0	8769(27)	141(10)	163(11)	1146(46)	−58(18)	0	0
Br(2)	0	5000	6370(32)	112(9)	169(10)	1676(61)	6(16)	0	0

(b) Light atoms ($\times 10^3$)

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
O(1)	246(9)	318(9)	581(9)	0.40(11)	O(8)	423(7)	212(9)	500(11)	0.66(11)
O(2)	209(9)	427(9)	1182(10)	0.59(12)	O(9)	239(9)	115(9)	571(9)	0.62(12)
O(3)	279(9)	227(9)	1248(10)	0.59(12)	B(1)	275(12)	326(12)	805(13)	0.17(13)
O(4)	78(9)	267(9)	1254(10)	0.69(12)	B(2)	187(12)	299(12)	1167(17)	0.54(14)
O(5)	283(10)	454(9)	844(11)	0.76(12)	B(3)	295(12)	218(12)	471(13)	0.39(15)
O(6)	388(10)	266(10)	847(10)	0.76(12)	B(4)	462(14)	236(15)	699(14)	0.72(18)
O(7)	185(9)	271(8)	928(9)	0.35(10)	B(5)	248(12)	497(12)	1031(12)	0.29(14)

the special positions (2*a* and 2*b* sites). The remaining O and B atoms were located on the successive Fourier maps. The isotropic refinements gave a conventional R value of 0.06 for both compounds; further refinements with anisotropic thermal factors for heavy atoms reduced the R and R_w values to 0.054 and 0.068 for 1967 reflections of $Eu_2B_5O_9Cl$ and 0.047 and 0.053 for 1979 reflections of $Eu_2B_5O_9Br$, where $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$. The weighting schemes of $w=(F_{max}/F_o)^2$ for $F_o>F_{max}$ and $w=1.0$ for $F_o\leqq F_{max}$ ($Eu_2B_5O_9Cl$, $F_{max}=20.0$; $Eu_2B_5O_9Br$, $F_{max}=40.0$), were employed. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[7] The final positional and thermal parameters are listed in Tables 2 and 3.††

Results and Discussion

Since the final parameters of $Eu_2B_5O_9Cl$ are almost equal to those of $Eu_2B_5O_9Br$, the two europium(II) haloborates were considered to be isostructural with each other.

The interatomic distances and angles of $Eu_2B_5O_9Cl$ are given in Table 4. There are two types of B atoms: in the first type [B(1), B(2), and B(3)], each B atom is tetrahedrally coordinated with four oxygens with B–O distances from 1.44 to 1.49 Å, while the second type [B(4) and B(5)] are triangularly coordinated borons with B–O distances from 1.30 to 1.41 Å. The O–B–O angles are about 110° for the tetrahedra and about 120° for the triangles. Three BO_4 tetrahedra and two BO_3 triangles form a B_5O_{12} group with sharing O atoms, and these groups are linked together with one another to form a three-dimensional $(B_5O_9)_\infty$ network. The projection of the $Eu_2B_5O_9Cl$ structure viewed along the c axis is shown in Fig. 1. The Eu and Cl atoms are alternately located in tunnels of the $(B_5O_9)_\infty$ network, and each Eu atom is almost entirely isolated from neighboring Eu atoms because of the $(B_5O_9)_\infty$ network for the a and b directions and Cl atoms for the c direction.

Each Eu atom has four nearest Eu neighbors with the mean interatomic distance of 4.387 Å and four next-nearest Eu neighbors with the mean interatomic

†† The F_o-F_c Table is kept as Document No. 8111 at the Chemical Society of Japan.

TABLE 4. INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN $Eu_2B_5O_9Cl$

(a) The $(B_5O_9)_\infty$ network			
B(1)-tetrahedron		B(2)-tetrahedron	
B(1)–O(1)	1.44(2)	B(2)–O(2)	1.49(3)
–O(5)	1.46(2)	–O(3)	1.48(3)
–O(6)	1.47(2)	–O(4)	1.45(3)
–O(7)	1.48(2)	–O(7)	1.49(3)
O(1)–B(1)–O(5)	106(1)	O(2)–B(2)–O(3)	112(2)
O(1)–B(1)–O(6)	112(1)	O(2)–B(2)–O(4)	109(2)
O(1)–B(1)–O(7)	111(1)	O(2)–B(2)–O(7)	110(2)
O(5)–B(1)–O(6)	110(2)	O(3)–B(2)–O(4)	108(2)
O(5)–B(1)–O(7)	112(1)	O(3)–B(2)–O(7)	107(2)
O(6)–B(1)–O(7)	106(1)	O(4)–B(2)–O(7)	111(2)
		B(3)-tetrahedron	
B(3)–O(1)	1.48(2)	O(1)–B(3)–O(3)	115(1)
–O(3)	1.47(2)	O(1)–B(3)–O(8)	111(1)
–O(8)	1.49(2)	O(1)–B(3)–O(9)	103(1)
–O(9)	1.49(2)	O(3)–B(3)–O(8)	104(1)
		O(3)–B(3)–O(9)	115(1)
		O(8)–B(3)–O(9)	110(1)
B(4)-triangle		B(5)-triangle	
B(4)–O(4)	1.41(3)	B(5)–O(2)	1.36(2)
–O(6)	1.30(3)	–O(5)	1.36(2)
–O(8)	1.40(3)	–O(9)	1.36(2)
O(4)–B(4)–O(6)	117(2)	O(2)–B(5)–O(5)	122(2)
O(4)–B(4)–O(8)	120(2)	O(2)–B(5)–O(9)	118(2)
O(6)–B(4)–O(8)	123(2)	O(5)–B(5)–O(9)	120(2)
(b) Eu–Eu distances[a]			
Nearest neighbors		Next-nearest neighbors	
Eu(1)–Eu(2)	4.026(1)	Eu(1)–Eu(1^{i})	5.731(1)
–Eu(2^{i})	5.036(1)		5.833(1)
–Eu(2^{ii})	4.421(1)	Eu(2)–Eu(2^{i})	5.461(2)
–Eu(2^{iii})	4.063(1)		5.899(2)
		Eu(1)–Eu(2)	5.473(1)
		–Eu(2^{i})	6.253(1)
(c) Eu–Cl and Eu–O distances			
Eu(1)-polyhedron		Eu(2)-polyhedron	
Eu(1)–Cl(1)	3.052(7)	Eu(2)–Cl(1)	3.022(7)
–Cl(2)	2.958(6)	–Cl(2)	2.967(6)
–O(1)	2.665(10)	–O(1)	2.667(10)
–O(2)	2.465(11)	–O(3)	2.888(10)
–O(3)	2.621(10)	–O(4)	2.851(12)
–O(5)	2.581(12)	–O(6)	2.559(12)
–O(6)	3.000(12)	–O(7)	2.552(10)
–O(7)	2.662(10)	–O(8)	2.617(12)
–O(9)	2.866(11)	–O(9)	2.801(11)

a) Symmetry code: Eu(1^{i}), ($\bar{x}$,$\bar{y}$,z); Eu(2^{i}), ($\bar{x}$,$\bar{y}$,z); Eu(2^{ii}), (1/2−x, 1/2+y, 1/2+z); Eu(2^{iii}), (1/2+x, 1/2−y, 1/2+z).

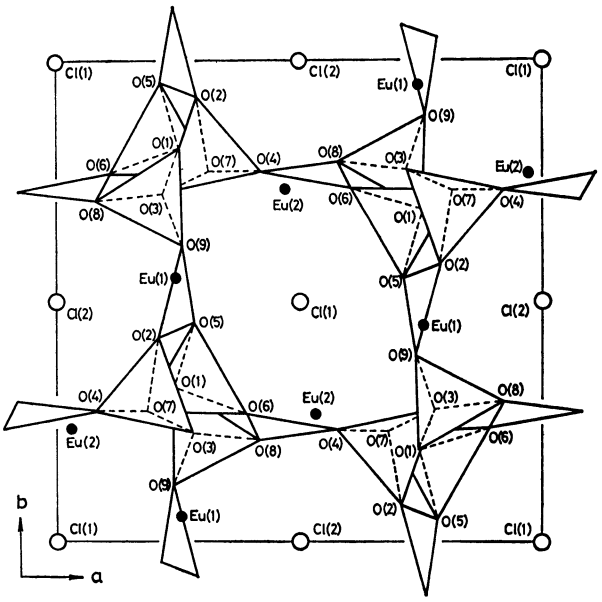

Fig. 1. A projection of the $Eu_2B_5O_9Cl$ structure along the c axis.

distance of 5.823 Å for the Eu(1) atom or 5.772 Å for the Eu(2) atom. These interatomic distances are long compared with those of other europium(II) compounds with magnetic transitions,[8] and are insufficient for the magnetic interactions between neighboring Eu^{2+} ions.[9] For example, the Eu–Eu distances in EuO (T_c=69 K) are 3.63 and 5.14 Å for the nearest and next-nearest Eu neighbors respectively. Therefore, $Eu_2B_5O_9X$ is paramagnetic even at low temperature.

The anion environments around Eu(1) and Eu(2) atoms in $Eu_2B_5O_9Cl$ are shown in Fig. 2. Both Eu(1) and Eu(2) are surrounded with two Cl atoms and seven O atoms to form $Eu(1)O_7Cl_2$ and $Eu(2)O_7Cl_2$ polyhedra with Eu–Cl distances from 2.985 to 3.052 Å and Eu–O distances from 2.465 to 3.000 Å.

Peters *et al.*[5] and Fouassier *et al.*[3] have obtained $M^{II}_2B_5O_9X$ phases in their attempts to prepare boracite ($M^{II}_3B_7O_{13}X$)-type compounds (M=Ca, Sr, Ba, Eu, and Pb). That is to say, these metal ions do not give boracite-type compounds. Each M^{2+} ion in boracites, which are formed in a ternary system, MO–MX_2–B_2O_3 (M=Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Cd), is surrounded by two X^- ions and four O^{2-} ions.[10] The fact that $M_2B_5O_9X$-type compounds are formed for M=Ca, Sr, Ba, Eu, and Pb may be due to their large ionic radii, since these ions hardly seem to occupy the sixfold sites of boracites.

The haloborates, $Eu_2B_5O_9Cl$ and $Eu_2B_5O_9Br$, give

TABLE 5. LUMINESCENCE AND STRUCTURAL DATA FOR Eu^{2+}-ACTIVATED Sr-COMPOUNDS

Compound	λ_{max}/nm[a]	(λ/2)/nm[b]	*Q.E.*/%[c]	*C.N.*[d]	Structural framework	Reference
$Sr_2B_5O_9Cl : Eu^{2+}$	425	30	50	9	$(B_5O_9)_\infty$ network	This work
$Sr_2B_5O_9Br : Eu^{2+}$	430	30	60	9	$(B_5O_9)_\infty$ network	This work
$SrB_2O_4 : Eu^{2+}$	367	20	≃2	8	$(BO_2)_\infty$ chain	2a
$SrB_4O_7 : Eu^{2+}$	367	20	40	9	$(B_4O_7)_\infty$ network	2a

a) λ_{max}=Peak position of the emission band at 300 K. b) λ/2=Half-width of emission band. c) *Q.E.*=Quantum efficiency of the Eu^{2+} concentration of a sample optimized under optimum excitation at 300 K. d) *C.N.*=Eu-coordination number.

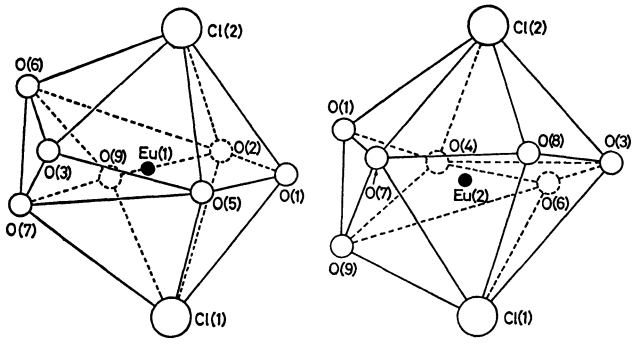

Fig. 2. Schematic illustrations of the $Eu(1)O_7Cl_2$ and $Eu(2)O_7Cl_2$ polyhedra in $Eu_2B_5O_9Cl$.

emissions at about 430 and 435 nm, and their Eu^{2+}-activated alkaline earth analogs are efficient phosphors. Since the ionic radius of the Sr^{2+} ion among alkaline earth cations is almost equal to that of the Eu^{2+} ion, strontium compounds are expected to be entirely isostructural with europium(II) analogs. Consequently, in order to discuss the relationship between the luminescence and structure of haloborates, we summarize the luminescence and structural properties for some Eu^{2+}-activated strontium compounds in Table 5.

The emission peak positions and shapes of Eu^{2+}-activated phosphors depend on the coordination numbers and symmetries of anions around Eu^{2+} ions, because the level of the $4f^65d$ excited state is affected by the crystal field. The haloborates, $Sr_2B_5O_9Cl : Eu^{2+}$ and $Sr_2B_5O_9Br : Eu^{2+}$, give emissions with a half-width of about 30 nm at 425—430 nm, while the emissions of $SrB_2O_4 : Eu^{2+}$ and $SrB_4O_7 : Eu^{2+}$ peak at about 367 nm. This must be because the symmetry of the EuO_7X_2 polyhedra (Fig. 2) is low compared with those[2a] of the EuO_8 and EuO_9 polyhedra in $SrB_2O_4 : Eu^{2+}$ and $SrB_4O_7 : Eu^{2+}$ because of the large X^- ions, although the Eu–O distances in these compounds are similar to one another (*e.g.*, 2.519 to 2.783 Å for EuB_2O_4[11] and 2.531 to 2.841 Å for EuB_4O_7[12]).

The quantum efficiencies of a series of Eu^{2+}-activated strontium borates greatly depend on the constructions of their borate units.[2] One of the quenching effects on Eu^{2+}-activated phosphors is a non-radiative process which proceeds by repeating the energy transfer *via* dipole-dipole interactions of Eu^{2+} ions.[13] Consequently, if the electrostatic shield effects of anions around the Eu^{2+} ions within them differ from one another, the values of their quantum efficiencies should vary with the degree of the shield effect. The Eu^{2+} ions in $SrB_2O_4 : Eu^{2+}$ are closely packed along $(BO_2)_\infty$ chains and are expected to interact easily with the neighboring Eu^{2+} ions on the (010) and (020) planes. The borate, $SrB_4O_7 : Eu^{2+}$, in which the Eu^{2+} ions are completely surrounded with the BO_4 tetrahedra of $(B_4O_7)_\infty$ network, gives a higher quantum efficiency than $SrB_2O_4 : Eu^{2+}$.

The quantum efficiency of $Sr_2B_5O_9X : Eu^{2+}$ is also very high compared with that of $SrB_2O_4 : Eu^{2+}$. The Eu^{2+} ions in $Sr_2B_5O_9X : Eu^{2+}$ are isolated from neighboring Eu^{2+} ions by the $(B_5O_9)_\infty$ network and X^- ions as well as those in $SrB_4O_7 : Eu^{2+}$; hence, the above-mentioned quenching effect can be expected to be small. Therefore, the high quantum efficiency of $Sr_2B_5O_9X : Eu^{2+}$ must be attributable to the arrangement of the borate units of the $(B_5O_9)_\infty$ network and X^- ions.

The authors wish to thank Dr. Noritake Yasuoka (Institute for Protein Research) and Professor Nobutami Kasai and Dr. Kunio Miki (Department of Applied Chemistry) for their helpful suggestions in connection with this study. The computations were carried out on an ACOS series 77 NEAC System 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

References

1) a) G. Blasse, *Phys. Status Solidi B*, **55**, K131 (1973); b) G. Blasse, "Structural and Bonding 26," Springer-Verlag, New York (1976), pp. 43—73.

2) a) K. Machida, G. Adachi, and J. Shiokawa, *J. Lumin.*, **21**, 101 (1979); b) K. Machida, G. Adachi, J. Shiokawa, M. Shimada, and M. Koizumi, *Inorg. Chem.*, **19**, 983 (1980).

3) C. Fouassier, A. Levasseur, and P. Hagenmuller, *J. Solid State Chem.*, **3**, 206 (1971).

4) K. Machida, T. Ishino, G. Adachi, and J. Shiokawa, *Mater. Res. Bull.*, **14**, 1529 (1979).

5) T. E. Peters and J. Baglio, *J. Inorg. Nucl. Chem.*, **32**, 1089 (1970).

6) T. Ashida, "The Universal Crystallographic Computing System-Osaka," The Computing Center, Osaka University (1979), pp. 53—59.

7) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72—102.

8) J. E. Greedan and G. J. McCarthy, *Mater. Res. Bull.*, **7**, 531 (1972).

9) T. R. McGuire and M. W. Shafer, *J. Appl. Phys.*, **35**, 984 (1964).

10) a) T. Ito, N. Morimoto, and R. Sadanaga, *Acta Crystallogr.*, **4**, 310 (1951); b) F. Jona, *J. Chem. Phys.*, **63**, 1750 (1959); c) F. Heide, G. Walter, and R. Urlau, *Naturwissenschaften*, **48**, 97 (1961); d) F. Heide and H. Beyrich, *Naturwissenschaften*, **52**, 181 (1965); e) J. Kobayashi, H. Schmid, and E. Ascher, *Phys. Status Solidi.*, **26**, 277 (1968); f) R. V. Pisarev, V. V. Druzhinin, S. D. Prochorova, N. N. Nesterova, and G. T. Andreeva, *Phys. Status Solidi*, **35**, 145 (1969); g) J. M. Trooster, *Phys. Status Solidi*, **32**, 179 (1969); h) W. J. Becker and G. Will, *Z. Kristallogr.*, **131**, 139 (1970); i) R. V. Pisrev, V. V. Druzhinin, N. N, Nesterova, S. D. Prochorova, and C. T. Andreeva, *Phys. Status Solidi*, **40**, 503 (1970); j) H. Schmid, *Phys. Status Solidi*, **37**, 209 (1970); k) T. A. Bither and H. S. Young, *J. Solid State Chem.*, **10**, 302 (1974).

11) K. Machida, G. Adachi, and J. Shiokawa, *Acta Crystallogr., Sect. B*, **35**, 149 (1979).

12) K. Machida, G. Adachi, and J. Shiokawa, *Acta Crystallogr., Sect. B*, **36**, 2008 (1980).

13) a) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953); b) G. Blasse, *Philips Res. Rep.*, **24**, 131 (1969); c) G. Blasse and A Bril, *Philips Tech. Rev.*, **31**, 304 (1970); d) A. L. N. Stevels and A. D. N. Schrama-de Pauw, *J. Electrochem. Soc.*, **123**, 691 (1976)